Available online at www.sciencedirect.com

SciVerse ScienceDirect

Procedia Engineering 44 (2012) 383 – 385

Procedia Engineering

www.elsevier.com/locate/procedia

Euromembrane Conference 2012

[OC17]

Modelling fluid flow in nanoporous membrane materials via non-equilibrium Molecular Dynamics

H. Frentrup*[1], C. Avendaño[2], M. Horsch[3], E.A. Müller[1]

[1]Imperial College London, UK, [2]Cornell University, USA, [3]Technische Universität Kaiserslautern, Germany

Layers of graphene oxide were recently fabricated into an active membrane layer. Pervaporation experiments through these membranes showed surprising results: the membrane proved to be impermeable to helium while allowing seemingly unimpeded pervaporation of water [8]. These results contradict current models of mass transfer in porous materials but can be explained by looking at effects on the nanoscale. There is a plethora of different approaches to predict the mass transfer in a porous membrane layer but with cutting-edge nanotechnology making its way into membrane applications, the approaches for predicting transport properties must keep up with innovation accordingly.

The most commonly applied methods rely either on classical hydrodynamics (Hagen-Poiseuille flow), a modification of transport in bulk phases (Dusty Gas model) or models based on kinetic theory (Knudsen diffusion) [2]. Experiments and molecular simulations have shown that the particular behaviour of fluids confined in nanopores differs greatly with what would be expected from traditional mass transfer models [6, 7]. The existing approaches struggle to incorporate a realistic description of nanoscale materials and the inherent molecular character to which nano-enhanced selective layers owe their remarkable properties [3]. In addition to pore size distribution and fluid-fluid interactions, solid-fluid interactions and the particular topology of porous structures (in the case of nanoscale materials) play an important role in influencing transport properties.

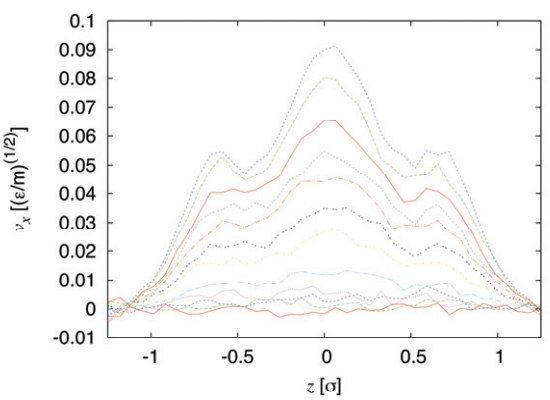

Figure 1: Velocity profile of a single monoatomic fluid in a highly attractive planar confinement at various external forces that mimic a pressure gradient. The pore width is wide enough to allow

doi:10.1016/j.proeng.2012.08.424

two molecular layers to form in it. The velocity profile is clearly different to a parabolic profile predicted by the Hagen-Poiseuille equation.

Molecular dynamics simulations internalise this molecular character in a realistic way and offer a method of predicting fluid flow through active membrane layers. These methodologies are particularly suitable to explore nanoconfined spaces, where the most interesting and challenging aspects of membrane transport take place.

We present a recently developed non-equilibrium Molecular Dynamics methodology to simulate fluid flow in nanoporous materials [5]. The method generates a steady-state flow through the application of an external force, which can be adjusted to either mimic a pressure gradient or gradient in chemical potential. We focus on presenting selectivity and permeability studies for carbon-based nanoporous materials, in particular graphene layers. Simulations were carried out for different variations in the design space. More specifically, we demonstrate the influence of a variation in porous design on fluid flow, namely a variation of the pore size, solid-fluid interactions. We analysed the effects for supercritical fluids in gaseous as well as dense fluid regions.

We compare the predictions of the simulations to the predictions of prevailing methods namely the Knudsen approach and the Hagen-Poiseuille model. We shed light on the mechanisms that provoke discrepancies and highlight the assumptions that render the existing approaches inaccurate, *c.f.* Figure 1 where the velocity profile in a slit nanopore is clearly non-classical. It becomes evident that the confinement has a decisive effect on the fluid properties. In pores on the scale of a few molecules, the fluid exhibits a particular structure where the density becomes non-uniform inside the pore [4, 5]. This has strong implications for viscous flow inside the pores as the viscosity of the fluid is not uniform either. In addition to pore size restrictions and fluid viscosity, we can show that pore adsorption and surface diffusion play a decisive role in mass transport through nanopores. It is worth noting that the solid-fluid interactions are to a large extent responsible for the breakdown of existing theoretical mass transport models.

It has been noted in the literature that in order to successfully adopt macroscopic mass transfer models to the nanoscale, a suitable constitutive model for shear stress and molecular momentum transfer should be developed [2]. We indicate how the presented method can be used to contribute to a development of such a relationship and how it can help to incorporate further molecular effects such as rugosity of the pore surface into transport models.

Compared to other molecular simulation methods that have been employed to study mass transfer phenomena in porous media, the approach we present here is in many respects superior. It is more robust as it is purely based on deterministic Molecular Dynamics simulation techniques, it has no particular simulation parameters that would alter transport dynamics and create spurious simulations results [1], and most notably it is not limited to simple model systems. The approach can easily be applied to systems with complex porous structures and elaborate macromolecular fluids. Moreover, there are no major obstacles to implement the approach in off-the-shelf Molecular Dynamics codes that are in widespread use.

References:

[1] Arya, G., Chang, H.-C., & Maginn, E. J. (2001). A critical comparison of equilibrium, non-equilibrium and boundary-driven molecular dynamics techniques for studying transport in microporous materials. *Journal of Chemical Physics*, *115*(17), 8112-8124.

[2] Bhatia, S. K., & Nicholson, D. (2006). Transport of simple fluids in nanopores: Theory and simulation. *AIChE Journal*, *52*(1), 29-38. doi:10.1002/aic.10580

[3] Bowen, W. R., & Welfoot, J. S. (2002). Modelling of membrane nanofiltration—pore size distribution effects. *Chemical Engineering Science*, *57*(8), 1393-1407. doi:10.1016/S0009-2509(01)00412-2

[4] Cai, Q., Biggs, M. J., & Seaton, N. A. (2008). Effect of pore wall model on prediction of diffusion coefficients for graphitic slit pores. *Physical Chemistry Chemical Physics*, *10*(18), 2519–2527. Retrieved from http://dx.doi.org/10.1039/B716648F

[5] Frentrup, H., Avendaño, C., Horsch, M., Salih, A., & Müller, E. A. (2011). Transport diffusivities of fluids in nanopores by non-equilibrium molecular dynamics simulation. *Molecular Simulation*, *in press*, doi:10.1080/08927022.2011.636813

[6] Holt, J. K., Park, H. G., Wang, Y., Stadermann, M., Artyukhin, A. B., Grigoropoulos, C. P., Noy, A., et al. (2006). Fast mass transport through sub-2-nanometer carbon nanotubes. *Science*, *312*(5776), 1034-1037. doi:10.1126/science.1126298

[7] Hummer, G., Rasaiah, J. C., & Noworyta, J. P. (2001). Water conduction through the hydrophobic channel of a carbon nanotube. *Nature*, *414*(6860), 188-190. doi:10.1038/35102535

[8] Nair, R. R., Wu, H. A., Jayaram, P. N., Grigorieva, I. V., & Geim, A. K. (2012). Unimpeded Permeation of Water Through Helium-Leak-Tight Graphene-Based Membranes. *Science*, *335*(6067), 442-444. doi:10.1126/science.1211694

Keywords: Nanopores, Molecular Dynamics, Non-Equilibrium, Transport diffusion